

Supporting Information

Stereocomplex Formation of Densely Grafted Brush Polymers

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1. Experimental Procedures

Materials

$(\text{H}_2\text{IMes})(\text{pyr})_2(\text{Cl})_2\text{RuCHPh}^1$ and *N*-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide,² were prepared as described previously. All solvents were purchased from VWR or Sigma-Aldrich. Ruthenium-based metathesis catalyst was obtained from Materia Inc. and stored in a drybox. D (+)-Lactide was obtained from BOC Sciences while other chemicals were bought from Sigma-Aldrich. Dry solvents were purified by passing them through solvent purification columns. Lactide monomers were purified by sublimation under vacuum. All other solvents and chemicals were used without further purification unless otherwise stated.

General information

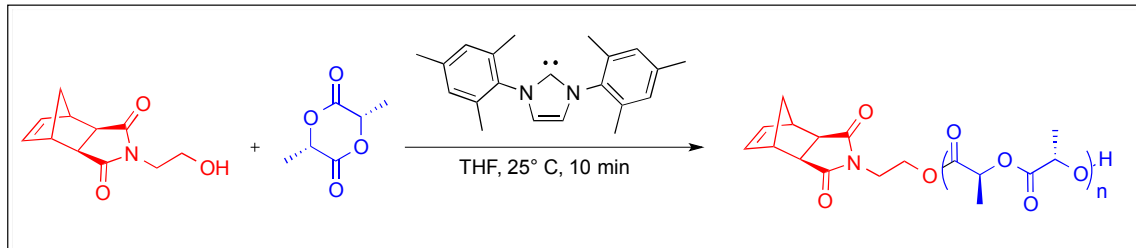
¹H NMR spectra were recorded at room temperature on a Varian Inova 500 (at 500 MHz). The NMR spectra were analyzed on MestReNova software and are reported relative to CDCl₃ (δ 7.26). NMR abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, dt = doublet of triplets.

Gel permeation chromatography (GPC) was carried out in THF on two Plgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a miniDAWN TREOS multiangle laser light scattering (MALLS) detector, a ViscoStar viscometer and Optilab rex differential refractometer (all from Wyatt Technology). The *dn/dc* values used for the poly(lactide) macromonomers were 0.050.

Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer DSC 7. Samples were heated to 125°C at 20°C/min, held at 25°C for 5 minutes and then cooled to 20°C at 10°C/min. The temperature was held at 20°C for 5 minutes before being reheated to 250°C at 10°C to determine the melting transition temperature. Finally, the sample was cooled back to room temperature at 20°C/min.

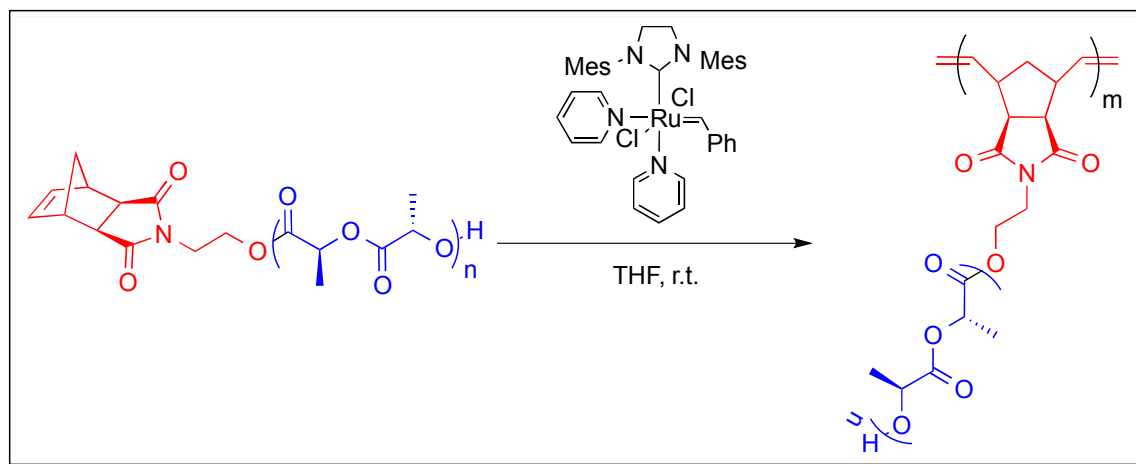
Optical rotations were measured in a solution of chloroform with a Jasco P-2000 polarimeter operating on a sodium D-line (589 nm) at 25°C, using a 10 cm path-length cell.

Synthesis



Representative procedure for the synthesis of Norbornene-Poly(lactide) (LMM-4)

The monomer, L-Lactide (2.00 g, 13.9 mmol) was added to a 40 mL scintillation vial and dissolved in 15 mL of dry THF. The initiator, *N*-(hydroxyethanyl)-*cis*-5-norbornene-*exo*-2,3-di-carboximide (35.7 mg, 0.172 mmol, 1 equiv) and the catalyst, 1,3-dimesitylimidazol-2-ylidene (9.6 mg, 31.5 μ mol) were added to a separate vial and dissolved in 3 mL of dry THF. Then the initiator/catalyst solution was added rapidly to the monomer solution and the whole solution allowed to stir for 10 min before being precipitated into MeOH. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 6.29 (br t, 2H), 5.32-5.00 (m, 177 H), 4.40-4.24 (m, 3H), 3.83-3.69 (m, 2H), 3.27 (s, 2H), 2.70 (br q, 2H), 1.73-1.39 (m, 532H), 1.25-1.23 (m, 1H). M_n (NMR) = 13.0 kg/mol. GPC-MALLS: M_n = 12.4 kg/mol, M_w/M_n = 1.11.



Representative procedure for the synthesis of a poly(lactide) brush copolymers (LBR-4)

The poly(lactide) macromonomer (157.8 mg, 12.1 μ mol) was weighed into a vial. The catalyst (2.8 mg, 3.85 μ mol) was added to a separate vial. The vials were brought into the drybox and the poly(lactide) macromonomer was dissolved in THF (500 μ L) while the catalyst was dissolved in 1.00 mL of THF. The catalyst solution (21 μ L, 0.081 μ mol) was injected via a microsyringe to the solution of macromonomers and the solution allowed to stir for 2 hours. The reaction was moved out of the dry box, quenched with butyl vinyl

ether and isolated by precipitation into MeOH. GPC-MALLS: $M_n = 2.15 \times 10^6$ g/mol, $M_w/M_n = 1.05$.

General procedure for preparation of blends

Equal amounts (w/w) of the complementary polymers (≈ 20 mg of each) were added to a small vial and subsequently dissolved in dichloromethane (≈ 2 mL). This solution was allowed to evaporate in the vial at room temperature and after drying under air it was put under high vacuum to ensure removal of the solvent.

2. Supplementary Tables

Table S1. GPC results for the macromonomers.

Sample	M_n (10^3 g/mol) ^a	M_n (10^3 g/mol) ^b	PDI ^b
L _{MM} -1	5.9	8.16	1.18
L _{MM} -2	8.6	10.6	1.16
L _{MM} -3	11.7	14.9	1.24
L _{MM} -4	13.0	12.4	1.11
D _{MM} -1	6.6	8.54	1.17
D _{MM} -2	8.6	10.5	1.15
D _{MM} -3	10.6	10.5	1.08
D _{MM} -4	17.4	16	1.05

^a Measured by NMR. ^b Measured by GPC

3. Supplementary Figures

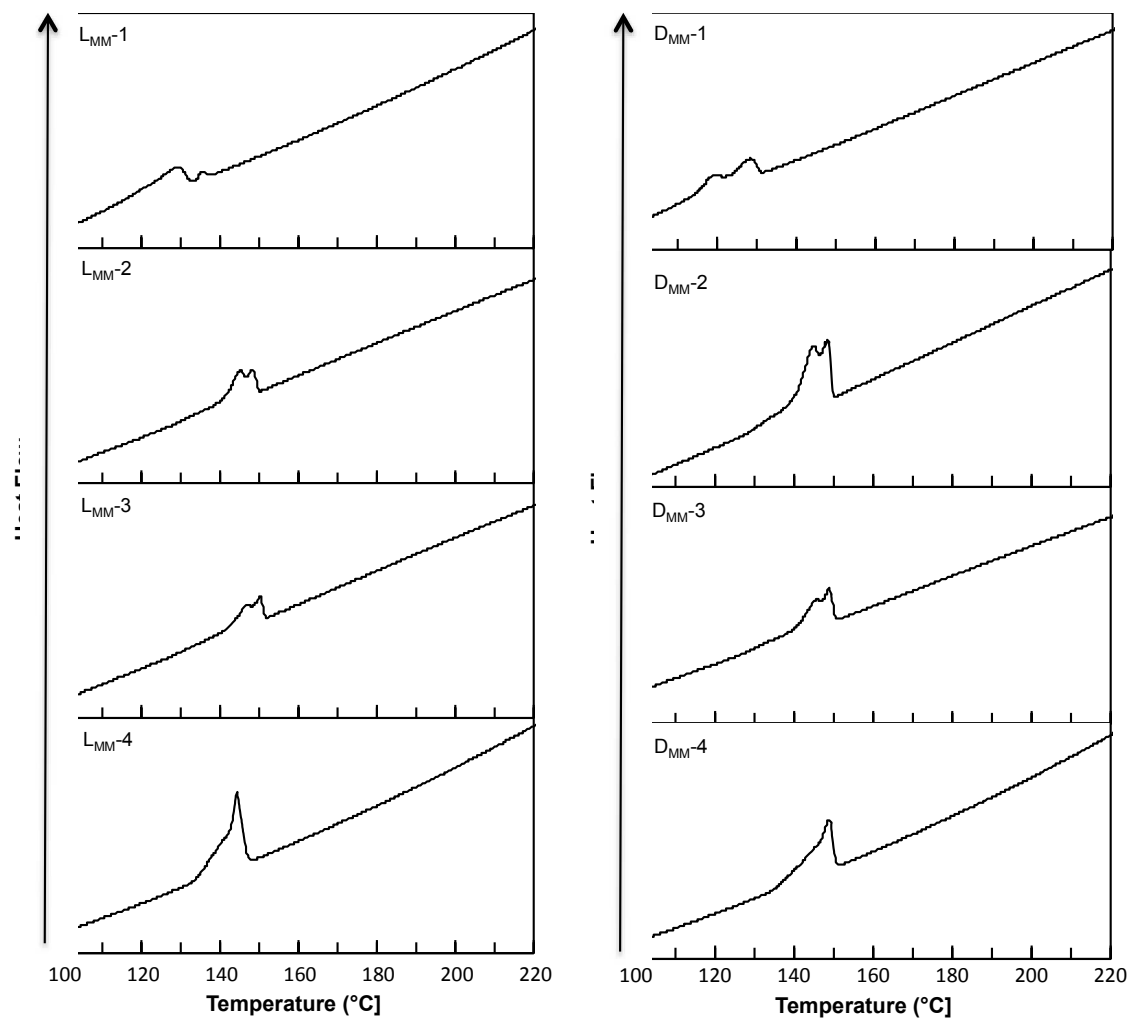


Figure S1. DSC traces of the heating cycle of the pure macromonomers.

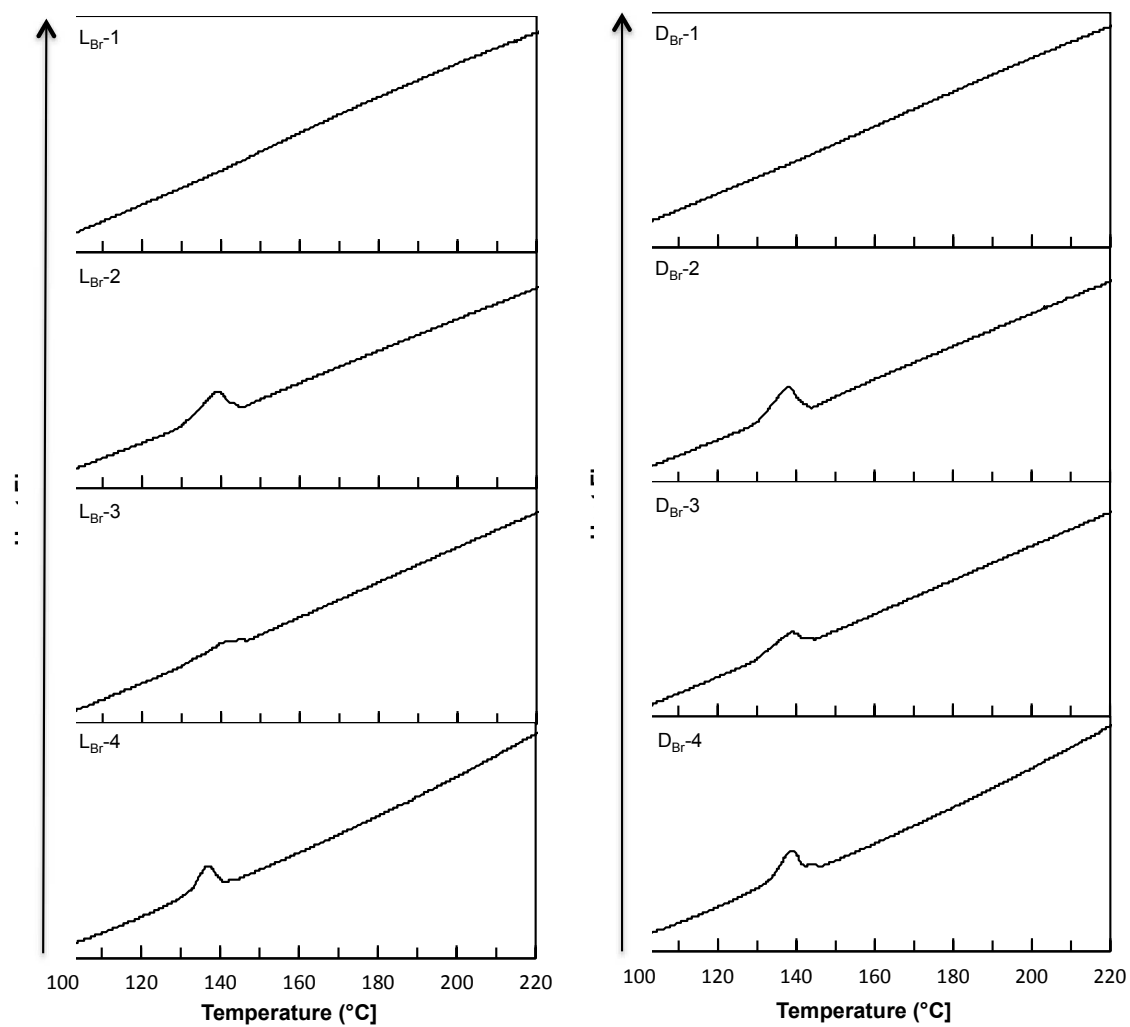


Figure S2. DSC traces of the heating cycle of the pure brush copolymers.

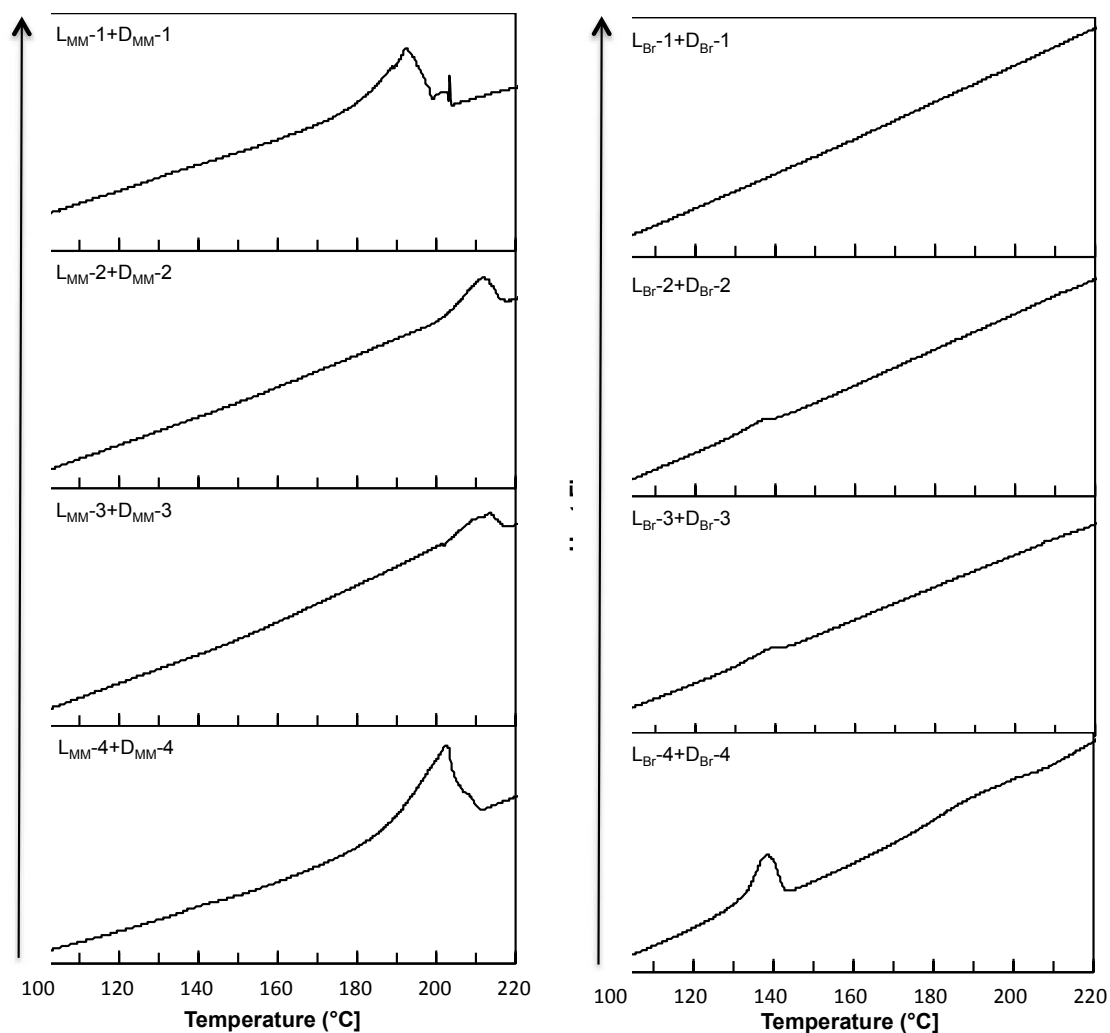


Figure S3. DSC traces of the heating cycle of the MM/MM blends (left) and the brush/brush blends (right)

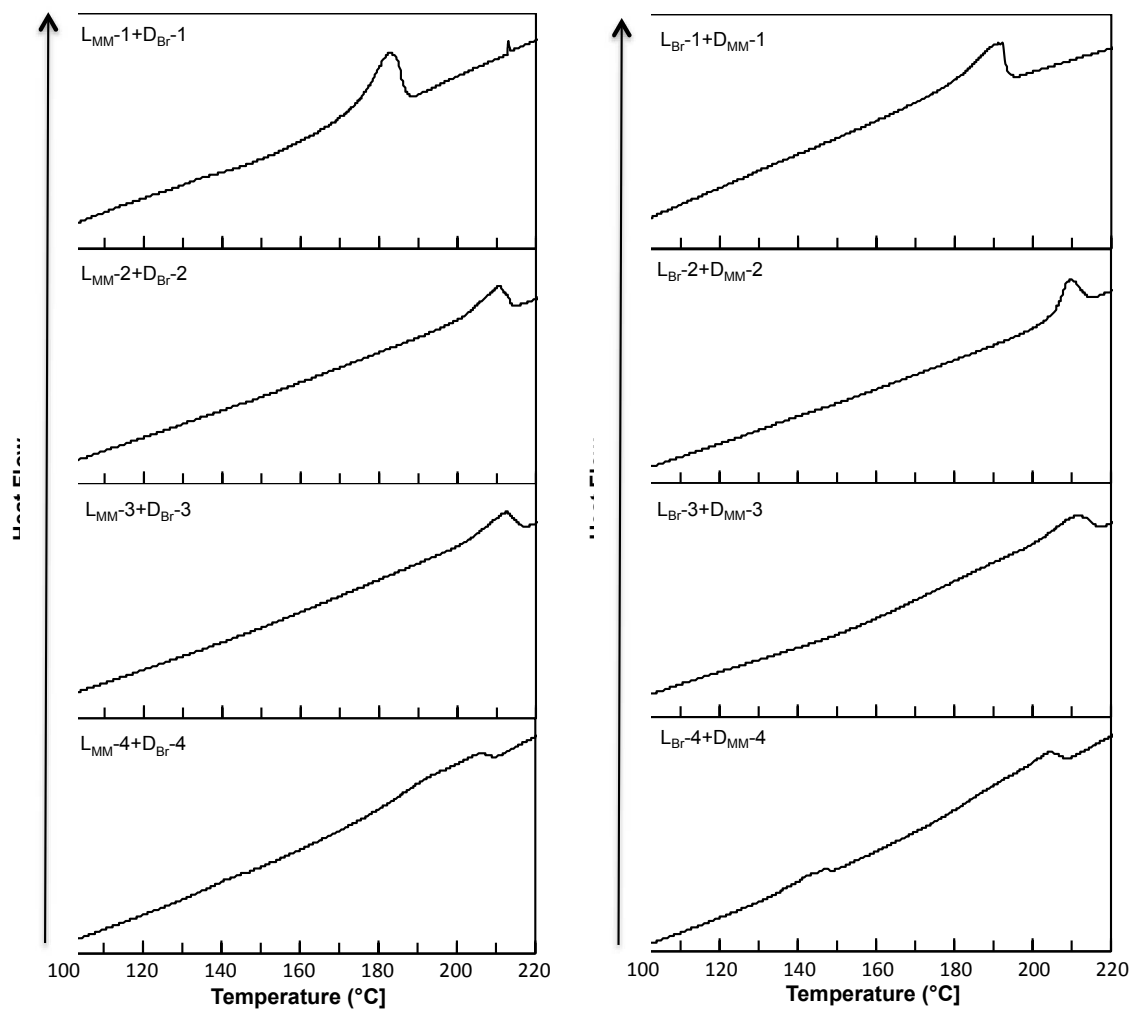


Figure S4. DSC traces of the heating cycle of the MM/brush blends.

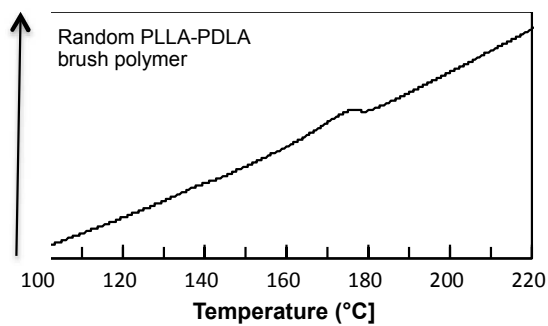


Figure S5. DSC trace of the heating cycle of the random PLLA-PDLA brush copolymer.

4. References

- (1) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. A Practical and Highly Active Ruthenium-Based Catalyst That Effects the Cross Metathesis of Acrylonitrile. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035–4037.
- (2) Matson, J. B.; Grubbs, R. H. Synthesis of Fluorine-18 Functionalized Nanoparticles for Use as in Vivo Molecular Imaging Agents. *J. Am. Chem. Soc.* **2008**, *130*, 6731–6733.